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Derwent Title: **Phosphorus - contg guanamines - react with formaldehyde to form flame resistant resins**

Original Title: [GB1343022A: PHOSPHORUS-CONTAINING GUANAMINES](#)

Assignee: **BRITISH OXYGEN CO LTD** Standard company
Other publications from [BRITISH OXYGEN CO LTD \(BRCO\)...](#)

Inventor: **None**

Accession/Update: **1974-02447V / 197402**

IPC Code: **C07F 9/40 ; C08G 9/28 ; D06M 15/64 ;**

Derwent Classes: **A60; E11; F06;**

Manual Codes: **A01-A02(Phosphorus containing monomers, condensants) , A01-E01(Triazines condensants) , A01-E05(Amines condensants) , A05-B(Aminoplasts [others]) , A06-B(Inorganic phosphorus polymers) , A09-A01(Non-flammability properties) , E05-G01(P-C bond, heterocyclic compound) , F03-C03(Chemical treatment of fabric products - flame proofing; fire retardants; melt proofing) , F05-A06C(Paper, cardboard by adding polymers, resins) , F05-B(Preservation and treatment of wood [plywood; other treatment])**

Derwent Abstract: **(GB1343022A) Ethylguanamines, useful in mfg. flame resistant resins for moulded plastics articles, or which impart flame resistance to wood, paper, laminates and textiles, have the formula:- (where R1 and R2 are each alkyl, aryl or aralkyl or halogenated derivs of these, and R1 may also be H), prep'd. by reacting dicyandiamide with a beta-(substd. phosphinyl)-propionitrile of formula:- at 50-200 degrees C in the presence of a basic catalyst. A prefd. cpd. is beta-(diethoxy-phosphinyl)-ethylguanamine.**

Family:	PDF	Patent	Pub. Date	Derwent Update	Pages	Language	IPC Code
	<input checked="" type="checkbox"/>	GB1343022A *		197402		English	C07F 9/40

INPADOC Legal Status: [Show legal status actions](#)

Priority Number:	Application Number	Filed	Original Title
	GB1970000010731	1970-03-05	PHOSPHORUS-CONTAINING GUANAMINES

Chemical Indexing Codes: [Show chemical indexing codes](#)

 [Polymer Multipunch Codes](#) [Show polymer multipunch codes](#)

 [Title Terms:](#) PHOSPHORUS CONTAIN REACT FORMALDEHYDE FORM FLAME RESISTANCE RESIN

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Derwent Searches: [Boolean](#) | [Accession/Number](#) | [Advanced](#)

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PATENT SPECIFICATION

(11) 1343022

1343022

(21) Application No. 10731/70 (22) Filed 5 March 1970
 (23) Complete Specification filed 19 April 1971
 (44) Complete Specification published 9 Jan. 1974
 (51) International Classification C07F 9/40//C08G 9/28 D06M 15/64
 (52) Index at acceptance

C2P 2E13 2E14 2E1L1 2E26B 7
 C3R 29M 29P 2M
 D1P 21Y 23Y 240 242 244 24Y 364 36Y 370 385 390
 39Y 49Y 505 50Y 510 51Y 562 567 56Y 570 581
 59X 59Y 605 610 622 62Y 649 64X 65Y 660 66Y
 795 L4

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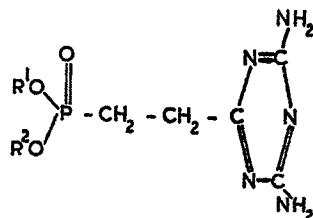


(54) PHOSPHORUS-CONTAINING GUANAMINES

(71) We, THE BRITISH OXYGEN COMPANY LIMITED, a British Company of Hammersmith House, London, W.6. England, do hereby declare the invention, for 5 which we pray that a patent may be granted to us, and the method by which it is performed, to be particularly described in and by the following statement:—

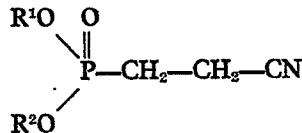
This invention relates to phosphorus-containing guanamines. In particular it relates 10 to a novel class of phosphorus-containing guanamines and to flame-resistant resins incorporating the said guanamines.

According to the present invention there 15 are provided novel substituted ethylguanamines of the formula:



wherein R¹ and R² may represent the same or 20 different radicals, R¹ representing an alkyl, aryl or aralkyl radical, or a halogen-substituted derivative thereof, or a hydrogen atom, and R² representing an alkyl, aryl or aralkyl radical, or a halogen-substituted derivative thereof.

25 The ethylguanamines can be prepared by reacting a β (substituted phosphinyl)-propionitrile of the formula:



30 wherein R¹ and R² have the meanings specified above, with dicyandiamide at a tempera-

ture within the range 50 to 200°C in the presence of a basic catalyst. The preferred propionitriles are β - (diethoxyphosphinyl) - propionitrile, β - (dimethoxyphosphinyl) - propionitrile and β - hydroxy(methoxy)phosphinyl - propionitrile which produce respectively β - (diethoxyphosphinyl) - ethylguanamine, β - (dimethoxyphosphinyl) - ethylguanamine and β - (hydroxy(methoxy)phosphinyl) - ethylguanamine.

The reaction is conveniently carried out 35 under reflux. Examples of suitable catalysts include alkali metal alcoholates, carbonates, hydroxides and amides.

The preparation of a β -(alkoxyphosphinyl)-propionitrile, from acrylonitrile and an alkyl phosphite, is described by A. N. Pudovic *et al* in Akad. Nauk. USSR 73, 327—30 (1950).

The invention also provides phosphorus-containing ethylguanamine/formaldehyde resins prepared from formaldehyde and the novel ethylguanamines of the present invention.

These resins can be prepared by reacting 55 one or more of the ethyl guanamines with formaldehyde at a temperature within the range 70 to 130°C and a pH within the range 5 to 9. The relative molar proportion of substituted ethylguanamine to formaldehyde is preferably within the range 1:2 to 1:8. If desired part of the ethylguanamine can be replaced by such a substance as urea, melamine or dicyandiamide. Conveniently the reaction is conducted under reflux and with stirring. The uncured resin so formed can be cured by heat treatment for example at a temperature within the range 100 to 200°C. The rate of curing can be increased by the use of an acid catalyst. The uncured resins are soluble in water and in lower aliphatic alcohols but the cured resins are insoluble in such solvents.

The resins, including those containing urea, 60 melamine, or dicyandiamide units, are themselves flame-resistant and can therefore be 65

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used to form articles, such as moulded plastics articles having flame resistance. They can also be used to impart flame resistance to materials or articles treated with them, especially to materials such as paper, textiles, fabrics, wood and laminates. When applied to textiles and fabrics they have been found to be advantageous in continuing to provide flame-resistance after washing. 40

5 When they are to be applied to an article or material the resins should be added in the uncured form and then cured by heat treatment. 45

10 The following examples illustrate various aspects of the invention. 50

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Example 1
128 g of β - (diethoxyphosphinyl) - propionitrile and 50 g of dicyandiamide were added to a solution of 1.4 g sodium in 150 ml 2-methoxyethanol. The mixture was refluxed for 4 hours and the suspension so formed was filtered at 100°C. The filtrate was allowed to cool and on standing formed a stiff paste. The paste was dispersed in 500 ml acetone and the resulting suspension filtered. The solid residue was washed with 1 litre acetone and dried to yield 85 g β - (diethoxyphosphinyl) - ethylguanamine. The combined filtrates and washings, on standing, deposited a further 44 g product which was recovered by filtration. The filtrate was then reduced in volume to 60 ml by distillation at sub-atmospheric pressure and dissolved in 100 mls acetone. On cooling the solution, 22 g of the guanamine crystallised out, giving a total yield of 151 g β - (diethoxyphosphinyl) - ethylguanamine. 55

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Example 2
1 mole of β - (diethoxyphosphinyl) - ethyl-

guanamine was added with stirring to 3 moles of formaldehyde at pH of 7.2. 40

The mixture was refluxed, with stirring, for 3 hours at 100°C and the resulting resin was cooled to room temperature. The resin was a clear, slightly yellow syrup, was soluble in water and had a solids content of 65.6%. After curing by heating for 1 hour at 150°C it was insoluble in water and in acetone. 45

Example 3

A sample of the uncured resin prepared according to Example 2 (solids content 65.6% by weight) was diluted with water to 10% solids content (by weight). Samples of cotton twill and filter paper were immersed in the solution and then dried at 60°C for 30 minutes followed by curing at 150°C for one hour. The cotton twill absorbed about 10% by weight of resin and the filter paper about 15% by weight. 50

The cotton twill and the filter paper were then subjected to a flame resistance test and the cotton twill was also subjected to a washing test. The results are given in the accompanying table. 55

Flame-resistance test

Strips of cotton twill or paper (measuring 15 cm by 1 cm) were exposed for 12 seconds to a constant gas flame (6.5 cm in height). The flame was applied at one end of the test strip. The duration of burning and the length of charred path were recorded. 60

Washing test cycle

A cotton twill sample was boiled for 15 minutes in water containing 0.5% by weight of liquid detergent. The sample was then thoroughly rinsed in cold water, and dried. 70

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TABLE

	Sample	No. of washing cycles	Duration of Burning (secs)	Length of Charred path (cm-max 15cm)
80	Untreated cotton twill	—	63	15.0
	Treated cotton twill	0	9	1.9
	"	1	23	4.4
85	"	3	47	11.4
	"	5	65	15.0
	Untreated filter paper	—	21	15.0
90	Treated filter paper	—	4	5.3

Example 4

Using the method of Example 1, 100 g of β - (dimethoxyphosphinyl) - propionitrile and 47.5 g of dicyandiamide were reacted to produce β - (dimethoxyphosphinyl) - ethylguanamine. The ethylguanamine was extracted by the method of Example 1 to give a total yield of 112 g. The extracted ethylguanamine was reacted with formaldehyde in the ratio 1 mole: 3 moles and under the conditions of Example 2 giving a clear syrup having a solids content 100

of 66.9% which was cured by heating at 150°C for 1 hour.

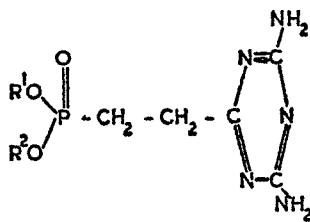
Example 5

5 Using the method of Example 1, 90 g of β - (hydroxy(methoxy)phosphinyl) - propionitrile and 48 g of dicyandiamide were reacted to produce β - (hydroxy(methoxy) phosphinyl) - ethylguanamine, in a total yield of 104 g.

10 The extracted ethylguanamine was reacted with formaldehyde in the ratio 1 mole: 3 moles and under the conditions of Example 2, giving a clear syrup having a solids content of 67.1% which was cured by heating 15 at 150°C for 1 hour.

WHAT WE CLAIM IS:—

1. Novel substituted ethylguanamines of the formula:



20 wherein R¹ and R² may represent the same or different radicals, R¹ representing an alkyl, aryl or aralkyl radical, or a halogen-substituted derivative thereof, or a hydrogen atom, and R² representing an alkyl, aryl or aralkyl radical, or a halogen-substituted derivative thereof.

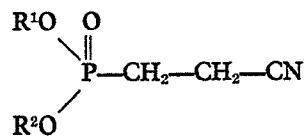
25 2. As a novel compound, β - (diethoxyphosphinyl) - ethylguanamine.

30 3. As a novel compound, β - (dimethoxyphosphinyl) - ethylguanamine.

35 4. As a novel compound, β - (hydroxy(methoxy)phosphinyl) - ethylguanamine.

5. A formaldehyde/substituted ethylguanamine resin prepared from formaldehyde and an ethylguanamine claimed in any preceding claim.

35 6. A method of preparing a substituted ethylguanamine as claimed in claim 1 which comprises reacting with dicyandiamide a β - (substituted phosphinyl) - propionitrile of the formula:



wherein R¹ and R² may represent the same or different radicals, R¹ representing an alkyl, aryl or aralkyl radical, or a halogen-substituted derivative thereof, or a hydrogen atom, and R² representing an alkyl, aryl, or aralkyl radical, or a halogen-substituted derivative thereof, at a temperature within the range 50 to 200°C in the presence of a basic catalyst.

7. A method as claimed in claim 6, wherein the reaction is carried out under reflux.

8. A method of preparing a formaldehyde substituted ethylguanamine resin which comprises reacting with formaldehyde one or more of the ethylguanamines claimed in any one of claims 1 to 4 at a temperature within the range 70 to 130°C and a pH within the range 5 to 9.

9. A method as claimed in claim 8 wherein the relative molar proportion of ethylguanamine to formaldehyde is within the range 1:2 to 1:8.

10. A method as claimed in claim 8 or claim 9 wherein part of the ethylguanamine is replaced by urea, melamine or dicyandiamide.

11. A method as claimed in any one claims 8 to 10 wherein the reaction is conducted under reflux and with stirring.

12. A method as claimed in any one of claims 8 to 11 wherein the reaction is followed by heat treatment to cure the resin.

13. A method as claimed in claim 12 wherein the treatment is conducted at a temperature within the range 100 to 200°C.

14. A method as claimed in claim 12 or 13 wherein the rate of curing is increased by the use of an acid catalyst.

15. A method of preparing a novel substituted ethylguanamine as claimed in claim 1, substantially as described in any one of Examples 1, 4 and 5 herein.

16. A method of preparing a formaldehyde substituted ethylguanamine resin as claimed in claim 8, substantially as described in any one of Examples 2, 4 and 5 herein.

For the Applicants,
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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.